Congress Research Lecture, Proceedings of the Fifth

U. S. National Congress of Applied Mechanics, 1966

On the Thermodynamics and Approximation Theory of Viscoelastic Materials

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Summary

A thermodynamic theory of materials with memory was developed in terms of difference histories by Coleman. The author has developed the theory in terms of past histories. The second law of thermodynamics in the form of the Clausius-Duhem inequality is taken as a restriction on processes as well as on constitutive equations. The Coleman-Noll approximation theory for materials with fading memory is developed for the thermodynamic theory.

A parallel development of the thermodynamic theory and the approximation theory is carried out for fluids with fading memory. For the zero-order approximation, the perfect fluid, the usual classical results are obtained. For the first-order approximation, corresponding to the Newtonian fluid, the constitutive equations differ from the traditional ones because of the possibility of certain additional terms; restrictions are obtained on the new coefficients as well as the classical restrictions on the usual coefficients. For the second-order approximation some restrictions are obtained on the material coefficients.

1. Introduction

Recently two fundamental and pioneering papers have appeared by Coleman [1, 2] on the development of the thermodynamics of materials with memory. Prior to this, the mechanics of materials with memory, ignoring thermodynamics, had been extensively developed; many references are given in references [1, 2]. An important development in the mechanics of materials with fading memory was an approximation theorem for functionals by Coleman and Noll [3].

A natural next development was the application of the approximation theory to the thermodynamics of materials with memory. In attempting to carry out this program, the author found that Coleman's theory in terms of difference histories [1, 2] was not entirely correct (see the appendix Sect. 10 of this paper). It appeared that the thermodynamic theory in terms of past histories could be a valid theory, however in [2, Sect. 9] Coleman only implies a summary of that theory. The author has developed the thermodynamic theory in terms of past histories in Sect. 3 of this paper. Furthermore, in this theory the Clausius-Duhem inequality is taken as a restriction on processes as well as on constitutive equations. In Sect. 4 the Coleman-Noll approximation theory for materials with memory is developed for the thermodynamic theory of Sect. 3. The foregoing results are specialized to fluids. The restrictions of the Clausius-Duhem inequality are determined for perfect fluids, linear fluids and the second-order fluid approximation.*

2. Review of preliminaries

For the most part this section will consist of a review of appropriate definitions and notations from Sects. 2,3,4 and 6 of Coleman [1].

Following Coleman [1, Sect. 2], we consider a

*See also Eringen [4] which treats general non-polar materials and specific constitutive equations different from those of this work.

N66 32143
Code 1
Cat 33 CR-76559
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body B with material points X. A thermodynamic process in B is described by eight functions of X and the time t. The values of these functions have the following physical interpretations:

(1) spatial position vector $\underset{\sim}{x} = \underset{\sim}{\chi}(X,t)$; here the function $\underset{\sim}{\chi}$, called the deformation function, describes a motion of the body.

(2) The symmetric stress tensor $\underset{\sim}{T} = \underset{\sim}{T}(X,t)$.

(3) The body force vector $\underset{\sim}{b} = \underset{\sim}{b}(X,t)$, per unit mass, exerted on B at X by the "external world".

(4) The specific internal energy $\epsilon = \epsilon(X,t)$, per unit mass.

(5) The specific entropy $\eta = \eta(X,t)$, per unit mass.

(6) The local absolute temperature $\theta = \theta(X,t)$, which is assumed to be positive: $\theta > 0$.

(7) The heat flux vector $\underset{\sim}{q} = \underset{\sim}{q}(X,t)$.

(8) The heat supply $r = r(X,t)$; this is the radiation energy, per unit mass and unit time, absorbed by B at X and furnished by the "external world".

Such a set of eight functions is called a thermodynamic process if and only if it is compatible with the law of balance of linear momentum and the law of balance of energy:

$$\int_{\partial V} \underset{\sim}{T}\,\underset{\sim}{n}\, da - \int_V \ddot{\underset{\sim}{x}}\, \rho dv = -\int_V \underset{\sim}{b}\, \rho dv \qquad (2.1)$$

$$\int_V \mathrm{tr}\{\underset{\sim}{T}\,\underset{\sim}{L}\} dv - \int_{\partial V} \underset{\sim}{q}\cdot\underset{\sim}{n}\, da - \int_V \dot{\epsilon}\, \rho dv = -\int_V r\, \rho dv \qquad (2.2)$$

where the conservation of mass is given by

$$\int_V \rho dv = \text{constant} \qquad (2.3)$$

Here ρ denotes the mass density; $\underset{\sim}{L} = \partial\dot{\underset{\sim}{x}}/\partial\underset{\sim}{x}$ is the velocity gradient; a superimposed dot denotes the material time derivative, i.e., the derivative with respect to t keeping X fixed; tr is the trace operator; V and dv indicate integration over the volume occupied by the body B and ∂V and da indicate integration over the surface of the space occupied by B.

The assumed symmetry of the stress tensor $\underset{\sim}{T}$ insures that the moment of momentum is automatically balanced. Couple stresses, body couples, and other mechanical interactions not included in $\underset{\sim}{T}$ or $\underset{\sim}{b}$ are are assumed to be absent.

In order to specify a thermodynamic process it suffices to prescribe the six functions $\underset{\sim}{\chi}, \underset{\sim}{T}, \epsilon, \underset{\sim}{q}, \eta$ and θ. The remaining functions $\underset{\sim}{b}$ and r are then determined by (2.1) and (2.2).

Here we depart somewhat from Coleman [1] and make a new definition. We define an allowable thermodynamic process for a body as a thermodynamic process which satisfies the Clausius-Duhem inequality [5]:

$$\int_V \dot{\eta}\, \rho dv - \left\{ -\int_{\partial V} \frac{1}{\theta}\, \underset{\sim}{q}\cdot\underset{\sim}{n}\, da + \int \frac{1}{\theta} r\, \rho dv \right\} \geq 0 \qquad (2.4)$$

We take (2.4) as a statement of the Second Law of Thermodynamics.

Following Coleman [1] again, it is often convenient to identify the material point X with its position vector $\underset{\sim}{X}$ in a fixed reference configuration R and to write

$$\underset{\sim}{x} = \underset{\sim}{\chi}(\underset{\sim}{X},t) \qquad (2.5)$$

The gradient $\underset{\sim}{F}$ of $\underset{\sim}{\chi}(\underset{\sim}{X},t)$ with respect to X, i.e.,

$$\underset{\sim}{F} = \underset{\sim}{F}(\underset{\sim}{X},t) = \partial\underset{\sim}{\chi}(\underset{\sim}{X},t)/\partial\underset{\sim}{X} \qquad (2.6)$$

is the deformation gradient tensor at $\underset{\sim}{X}$ (i.e., at X) relative to the configuration R. It is well known that

$$\dot{\underset{\sim}{F}} = \underset{\sim}{L}\,\underset{\sim}{F}, \text{ i.e., } \underset{\sim}{L} = \dot{\underset{\sim}{F}}\,\underset{\sim}{F}^{-1} \qquad (2.7)$$

It is assumed that $\underset{\sim}{\chi}(\underset{\sim}{X},t)$ is always smoothly invertible in its first variable, i.e., that the inverse $\underset{\sim}{F}^{-1}$ of $\underset{\sim}{F}$ exists, or, equivalently, that $\det \underset{\sim}{F} \neq 0$.

Since $\partial\theta/\partial\underset{\sim}{x}$ occurs often Coleman introduced the abbreviation

$$\underset{\sim}{g} \equiv \partial\theta/\partial\underset{\sim}{x} \qquad (2.8)$$

The mass density ρ is determined by $\underset{\sim}{F}$ through the equation

$$\rho = \rho_r / |\det \underset{\sim}{F}| \qquad (2.9)$$

where ρ_r is a positive number, constant in time and equal to the mass density in the reference configuration R.

The specific free energy ψ is defined by

$$\psi = \epsilon - \theta\eta \qquad (2.10)$$

Using (2.2), (2.7) and (2.10), under appropriate smoothness assumptions the differential equation form of the Clausius-Duhem inequality is

$$\theta\gamma \equiv -\dot{\psi} + \frac{1}{\rho}\,\mathrm{tr}\{\underset{\sim}{F}^{-1}\,\underset{\sim}{T}\,\dot{\underset{\sim}{F}}\} - \eta\dot{\theta} - \frac{1}{\rho\theta}\,\underset{\sim}{q}\cdot\underset{\sim}{g} \geq 0 \quad (2.11)$$

where γ is called the specific rate of entropy production.

Denote any of the above functions of X and t by $\varphi(t)$. The function

$$\varphi^t(s) = \varphi(t - s), \quad 0 \leq s < \infty \qquad (2.12)$$

is called the history of φ at X up to time t.

Next consider a function $\beta(t)$ which is determined by $\varphi^t(s)$ for all values of s satisfying (2.12), that is $\beta(t)$ is a functional of $\varphi^t(s)$. In this paper we shall indicate functionals by the following notation:

$$\beta(t) = f(\varphi^t(s)) \qquad (2.13)$$

In using (2.13) it will be understood that whenever a function of s, in this case $\varphi^t(s)$, appears as the argument of a function, f, then f is to be considered a functional of $\varphi^t(s)$.

A material is defined by a set of constitutive assumptions, which are restrictions on thermodynamic processes. Following Coleman we define a simple material as one for which

$$f = f(\underset{\sim}{F}^t(s),\theta^t(s);\,\underset{\sim}{g}), \quad f \equiv \psi,\eta,\underset{\sim}{T},\underset{\sim}{q} \quad (2.14a,b,c,d)$$

Following Coleman a thermodynamic process is said to be admissible in B if it is compatible with (2.14) at each point X of B and at all times t. Thus an allowable admissible thermodynamic process is an admissible thermodynamic process that is allowed by the Clausius-Duhem inequality. Coleman [1] shows that the following is an admissible thermodynamic process: $\underset{\sim}{x} = \underset{\sim}{\chi}(X,t)$ and $\theta = \theta(X,t)$ are assigned for all t and X in B.

Coleman [1] introduces the following compact notation. We denote by $\underset{\sim}{\Lambda}$ the ordered pair $(\underset{\sim}{F},\theta)$, where $\underset{\sim}{F}$ is any tensor and θ any scalar:

$$\underset{\sim}{\Lambda} = (\underset{\sim}{F},\theta) \qquad (2.15)$$

Let α be a scalar, the product $\alpha\underset{\sim}{\Lambda} = \underset{\sim}{\Lambda}\alpha$ is defined to be

$$\alpha\underset{\sim}{\Lambda} = (\alpha\underset{\sim}{F},\,\alpha\theta) \qquad (2.16)$$

Let $\underset{\sim}{\Lambda}_1 = (\underset{\sim}{F}_1,\theta_1)$ and $\underset{\sim}{\Lambda}_2 = (\underset{\sim}{F}_2,\theta_2)$. The sum $\underset{\sim}{\Lambda}_1 + \underset{\sim}{\Lambda}_2$ is defined to be

$$\underset{\sim}{\Lambda}_1 + \underset{\sim}{\Lambda}_2 = (\underset{\sim}{F}_1 + \underset{\sim}{F}_2,\ \theta_1 + \theta_2) \qquad (2.17)$$

The scalar-multiplication and addition so defined make the set of all ordered pairs (2.15) a vector space of dimension ten. An inner product $\cdot$ and a norm $\| \|$ are defined by

$$\underset{\sim}{\Lambda}_1 \cdot \underset{\sim}{\Lambda}_2 = \mathrm{tr}(\underset{\sim}{F}_1\underset{\sim}{F}_2^T) + \theta_1\theta_2, \quad \|\underset{\sim}{\Lambda}\| = \sqrt{\underset{\sim}{\Lambda}\cdot\underset{\sim}{\Lambda}} \qquad (2.18)$$

If $\underset{\sim}{F}^t(s)$ is the deformation gradient history and $\theta^t(s)$ is the temperature history, then $\underset{\sim}{\Lambda}^t(s)$ defined by

$$\underset{\sim}{\Lambda}^t(s) = \underset{\sim}{\Lambda}(t - s) = (\underset{\sim}{F}^t(s),\ \theta^t(s)),\ 0 \leq s < \infty \quad (2.19)$$

is called the total history or simply the history. We define $\underset{\sim}{\Lambda}$ to be

$$\underset{\sim}{\Lambda} = \underset{\sim}{\Lambda}(t) = \underset{\sim}{\Lambda}^t(0) \qquad (2.20)$$

Using this compact notation we can rewrite (2.14) as

$$f = f(\underset{\sim}{\Lambda}^t(s);\underset{\sim}{g}), \quad f \equiv \psi,\eta,\underset{\sim}{T},\underset{\sim}{q} \qquad (2.21a,b,c,d)$$

Introducing the generalized stress

$$\underset{\sim}{\Sigma} = \left(\frac{1}{\rho}\,\underset{\sim}{T}\,\underset{\sim}{F}^{-T},\ -\eta\right) = \left(\frac{1}{\rho}(\underset{\sim}{F}^{-1}\underset{\sim}{T})^T,\ -\eta\right) \qquad (2.22)$$

we see that by (2.18) the Clausius-Duhem inequality (2.11) can be rewritten as

$$\theta\gamma \equiv -\dot{\psi} + \underset{\sim}{\Sigma}\cdot\dot{\underset{\sim}{\Lambda}} - \frac{1}{\rho\theta}\underset{\sim}{q}\cdot\underset{\sim}{g} \geq 0 \qquad (2.23)$$

where

$$\dot{\underset{\sim}{\Lambda}} = (\dot{\underset{\sim}{F}},\dot{\theta}) \qquad (2.24)$$

It follows from (2.22) and (2.21b), (2.21c) that $\underset{\sim}{\Sigma}$ is given by a functional of $\underset{\sim}{\Lambda}^t(s)$ which is also a function of $\underset{\sim}{g}$, that is

$$\underset{\sim}{\Sigma} = \underset{\sim}{\Sigma}(\underset{\sim}{\Lambda}^t(s);\ \underset{\sim}{g}) \qquad (2.25)$$

3. Thermodynamic Theory in terms of Past Histories

The past history $\underset{\sim}{\Lambda}_r^t(s)$ is defined by Coleman [2, Sect. 9] as the history $\underset{\sim}{\Lambda}^t(s)$ restricted to the open interval $0 < s < \infty$, that is,

$$\underset{\sim}{\Lambda}_r^t(s) = \underset{\sim}{\Lambda}^t(s),\ 0 < s < \infty \qquad (3.1)$$

For the time being we will assume of $\underset{\sim}{\Lambda}_r^t(s)$ only that it have a limit at $s = 0$ and we define

$$\underset{\sim}{\Lambda}_r = \lim_{s\to 0}\underset{\sim}{\Lambda}_r^t(s) \qquad (3.2)$$

The history $\underset{\sim}{\Lambda}^t(s)$ is allowed to have a jump at $s = 0$ so that in general

$$\boldsymbol{\Lambda} \neq \boldsymbol{\Lambda}_r \tag{3.3}$$

where $\boldsymbol{\Lambda}$ is defined by (2.20).

Following Coleman [2, Sect. 9] we define a new functional for the free energy ψ by means of

$$\psi(t) = \psi(\boldsymbol{\Lambda}^t(s);\ \mathbf{g}(t)) = \psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda}(t), \mathbf{g}(t)) \tag{3.4}$$

where the new functional form is indicated by $\psi(\ ;\ ,\ )$ as compared with the old form $\psi(\ ;\ )$.

Now we can see that the time derivative of ψ is required for use in (2.23). Let us then proceed to formally take the time derivative of the last term in (3.4) and then make the assumptions required to justify such a procedure. By definition

$$\dot{\psi}(t) = \lim_{k \to 0} \frac{1}{k} \left[\psi(t + k) - \psi(t)\right] \tag{3.5}$$

Then by (3.4) we have

$$\psi(t + k) = \psi(\boldsymbol{\Lambda}_r^{t+k}(s);\ \boldsymbol{\Lambda}(t + k),\ \mathbf{g}(t + k)) \tag{3.6}$$

Now because of the possible jump in $\boldsymbol{\Lambda}^t(s)$ at $s = 0$ as indicated by (3.3), $\boldsymbol{\Lambda}(t)$ and $\mathbf{g}(t)$ can only have derivatives for positive k, that is

$$\boldsymbol{\Lambda}(t + k) = \boldsymbol{\Lambda}(t) + k\dot{\boldsymbol{\Lambda}}(t) + o(k), \quad k > 0 \tag{3.7a}$$

$$\mathbf{g}(t + k) = \mathbf{g}(t) + k\dot{\mathbf{g}}(t) + o(k), \quad k > 0 \tag{3.7b}$$

Formally we can make a Taylor series approximation to $\boldsymbol{\Lambda}_r^{t+k}(s)$, namely

$$\begin{aligned} \boldsymbol{\Lambda}_r^{t+k}(s) &= \boldsymbol{\Lambda}_r^t(s) + k \frac{d}{dt} \boldsymbol{\Lambda}_r^t(s) + o(k,s) \\ &= \boldsymbol{\Lambda}_r^t(s) - k \frac{d}{ds} \boldsymbol{\Lambda}_r^t(s) + o(k,s) \end{aligned} \tag{3.8}$$

where we have made use of (2.19) and where $o(k,s)$ indicates that the error term depends on s as well being small order k. Now since $\boldsymbol{\Lambda}^t(s)$ is allowed to suffer a jump discontinuity at $s = 0$, then at a later instant $t + k$ ($k > 0$) the function $\boldsymbol{\Lambda}_r^{t+k}(s)$ has a jump at $s = k$. Hence the expansion (3.8) will only be meaningful for $s > k$. This restriction has to be kept in mind in the limit as $s \to 0$. To be consistent with the assumption that the argument function $\boldsymbol{\Lambda}_r^{t+k}(s)$ of (3.6) satisfy (3.2) we must assume as $s \to 0$ that the derivative $d\boldsymbol{\Lambda}_r^t(s)/ds$ exist and that $o(k,s)$ exist.

We see from (3.5), (3.6) and (3.7) that we must assume that ψ is differentiable in $\boldsymbol{\Lambda}$ and $\mathbf{g}$. That is, there exist functionals $\partial_{\boldsymbol{\Lambda}}\psi$ and $\partial_{\mathbf{g}}\psi$ such that

$$\begin{aligned} \psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda} + \boldsymbol{\Omega},\ \mathbf{g}) = {} & \psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda},\ \mathbf{g}) + \\ & + \partial_{\boldsymbol{\Lambda}}\psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda},\ \mathbf{g})\cdot\boldsymbol{\Omega} + o(\|\boldsymbol{\Omega}\|) \end{aligned} \tag{3.9}$$

$$\begin{aligned} \psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda},\ \mathbf{g} + \mathbf{v}) = {} & \psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda}, \mathbf{g}) + \\ & + \partial_{\mathbf{g}}\psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda},\ \mathbf{g})\cdot\mathbf{v} + o(\|\mathbf{v}\|) \end{aligned} \tag{3.10}$$

where $\boldsymbol{\Omega}$ is an arbitrary element in the ten-dimensional vector space and $\mathbf{v}$ is an arbitrary vector.

We also see from (3.5), (3.6) and (3.8) that ψ must be differentiable in the function $\boldsymbol{\Lambda}_r^t(s)$, that is there exists a functional $\delta\psi$ such that

$$\begin{aligned} \psi(\boldsymbol{\Lambda}_r^t(s) + \boldsymbol{\Gamma}(s);\ \boldsymbol{\Lambda},\ \mathbf{g}) = {} & \psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda},\ \mathbf{g}) + \\ & + \delta\psi(\boldsymbol{\Lambda}_r^t(s);\ \boldsymbol{\Lambda},\ \mathbf{g} | \boldsymbol{\Gamma}(s)) + o(\|\boldsymbol{\Gamma}(s)\|_h) \end{aligned} \tag{3.11}$$

where in order to be consistent with (3.2) $\boldsymbol{\Gamma}(s)$ must have a limit as $s \to 0$, where $\delta\psi$ is a linear functional of $\boldsymbol{\Gamma}(s)$, and, $\|\boldsymbol{\Gamma}(s)\|_h$ is a suitable norm of $\boldsymbol{\Gamma}(s)$. As discussed by Coleman [1], we may consider a class of materials whose memory fades gradually in time. In that case a suitable norm $\|\boldsymbol{\Gamma}(s)\|_h$ is one whose value depends more on $\boldsymbol{\Gamma}(s)$ for small s than for large s. Such a norm is

$$\|\boldsymbol{\Gamma}(s)\|_h = \left[\int_0^\infty \|\boldsymbol{\Gamma}(s)\|^2 h(s)^2 ds\right]^{\frac{1}{2}} \tag{3.12}$$

where the <u>influence function</u> $h(s)$, $0 \le s < \infty$ is a positive, monotone-decreasing, continuous function which goes to zero rapidly as $s \to \infty$. We summarize the above statements concerned with differentiation with respect to $\boldsymbol{\Lambda}_r^t(s)$ as an

<u>Assumption of fading memory</u>. We consider a class of simple materials for which the specific free energy is differentiable in the past history in terms of the norm (3.12) where the influence function decreases rapidly to zero as $s \to \infty$. We note especially that the past history must have a limit as $s \to 0$, but that it may otherwise be badly behaved so long as the norm (3.12) exists.

A simple material for which the above assumption of fading memory holds will be called a <u>viscoelastic material</u>.

Now returning to the problem of evaluating (3.5), we substitute (3.7a), (3.7b) and (3.8) into (3.6); we then use (3.9), (3.10) and (3.11) and carry out formally the limiting process of (3.5) and finally get

$$\begin{aligned}\dot{\psi}(t) = -\,\delta\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g} \mid \tfrac{d}{ds}\, \underset{\sim}{\Lambda}^t_r(s)) \,+ \\ +\, \partial_{\Lambda}\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}) \cdot \dot{\underset{\sim}{\Lambda}} + \partial_{\underset{\sim}{g}}\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}) \cdot \dot{\underset{\sim}{g}}\end{aligned} \tag{3.13}$$

where the derivatives $\dot{\underset{\sim}{\Lambda}}(t)$, $\dot{\underset{\sim}{g}}(t)$ and hence $\dot{\psi}(t)$ may only exist in the positive direction. In carrying out the above procedure it is necessary to make a weak additional assumption that*

$$\lim_{k\to 0} \frac{1}{k}\, \delta\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda}(t),\, \underset{\sim}{g}(t) \mid o(k,s)) = 0 \tag{3.14}$$

We also write the entropy, stress, heat flux and generalized-stress functionals in terms of the past history $\underset{\sim}{\Lambda}^t_r(s)$:

$$f = f(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}),\quad f \equiv h, \underset{\sim}{T}, \underset{\sim}{q}, \underset{\sim}{\Sigma} \tag{3.15a,b,c,d}$$

Then substituting (3.13), (3.15c) and (3.15d) in the inequality (2.23) we get

$$\begin{aligned}\theta\gamma = \left\{ \underset{\sim}{\Sigma}\, (\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}) - \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g})\right\} \cdot \dot{\underset{\sim}{\Lambda}} \,+ \\ +\, \delta\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g} \mid \tfrac{d}{ds}\underset{\sim}{\Lambda}^t_r(s)) - \tfrac{1}{\rho\theta}\, \underset{\sim}{q}(\underset{\sim}{\Lambda}^t_r(s);\underset{\sim}{\Lambda},\underset{\sim}{g})\cdot \underset{\sim}{g} \,- \\ -\, \partial_{\underset{\sim}{g}}\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}) \cdot \dot{\underset{\sim}{g}} \geq 0\end{aligned} \tag{3.16}$$

Now Coleman [1, Sect. 4] has shown that at a given material point X and time t we can arbitrarily choose the past history $\underset{\sim}{\Lambda}^t_r(s)$ and the quantities $\underset{\sim}{\Lambda}(t)$, $\underset{\sim}{g}(t)$, $\dot{\underset{\sim}{g}}(t)$ and be certain that there exists at least one admissible thermodynamic process corresponding to this. From our discussion in this section, $\dot{\underset{\sim}{g}}(t)$ may only be defined in the positive direction for jump histories. Also from our discussion it is clear that $\dot{\underset{\sim}{\Lambda}}(t)$ in the positive direction may be chosen arbitrarily for jump histories.

Since $\dot{\underset{\sim}{g}}$ can be assigned arbitrarily in (3.16) with everything else held fixed it is clear (see [1, Sect. 6] for a detailed argument) that

$$\psi = \psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda}) \tag{3.17}$$

That is, the specific free energy ψ cannot be a function of the temperature gradient. Thus (3.16) reduces to

$$\begin{aligned}\theta\gamma = \left\{ \underset{\sim}{\Sigma}\, (\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}) - \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda})\right\} \cdot \dot{\underset{\sim}{\Lambda}} \,+ \\ +\, \delta\psi(\underset{\sim}{\Lambda}^t_r(s);\underset{\sim}{\Lambda} \mid \tfrac{d}{ds}\underset{\sim}{\Lambda}^t_r(s)) - \tfrac{1}{\rho\theta}\, \underset{\sim}{q}(\underset{\sim}{\Lambda}^t_r(s);\underset{\sim}{\Lambda},\, \underset{\sim}{g}) \cdot \underset{\sim}{g} \geq 0\end{aligned} \tag{3.18}$$

Since $\dot{\underset{\sim}{\Lambda}}$ can be assigned arbitrarily holding everything else fixed we conclude that

$$\underset{\sim}{\Sigma} = \underset{\sim}{\Sigma}\, (\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda}) = \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda}) \tag{3.19}$$

We observe that the generalized stress cannot be a function of the temperature gradient $\underset{\sim}{g}$, that the generalized stress is the derivative of the specific free energy with respect to the present value of the total history, $\underset{\sim}{\Lambda}$, and that the assumption of fading memory must apply to the generalized stress. Next we can assign $\underset{\sim}{g}$ the value zero independently of the other quantities and get

$$\theta\sigma \equiv \delta\psi(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda} \mid \tfrac{d}{ds}\, \underset{\sim}{\Lambda}^t_r(s) \geq 0 \tag{3.20}$$

That is, the <u>internal dissipation</u> σ [1, Sect. 6] cannot be negative. Then finally we must have

$$\underset{\sim}{q}(\underset{\sim}{\Lambda}^t_r(s);\, \underset{\sim}{\Lambda},\, \underset{\sim}{g}) \cdot \underset{\sim}{g} \leq \rho\theta^2\sigma \tag{3.21}$$

The results (3.19), (3.20) and (3.21) are similar to those obtained by Coleman [1, Sect. 6]. The equivalent of our equation (3.19) is also given by Coleman and Gurtin [6]. A jump in $\dot{\underset{\sim}{\Lambda}}$ is, according to Coleman and Gurtin, a <u>thermo-mechanical acceleration wave</u>. Thus equations (3.19) to (3.21) may be said to hold for materials in which acceleration waves are allowed. However for a given class of constitutive equations the allowance of acceleration waves may impose intolerable restrictions on the constitutive equations. Let us now examine the inequality (3.18) with the assumption that

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*Dr. C.-C. Wang has kindly pointed out to me that Professor V. J. Mizel and he proved in a private discussion the following much more complete theorem regarding (3.13); If ψ satisfies (3.11) for all $\underset{\sim}{\Gamma}(s)$ which obeys $\|\underset{\sim}{\Gamma}(s)\|_h < \infty$ and, if one writes $\underset{\sim}{\Lambda}_r(s) + \underset{\sim}{\Gamma}(s) = (\underset{\sim}{A}(s), b(s))$, det $\underset{\sim}{A}(s) \neq 0$, $b(s) > 0$ then (3.13) holds for all $\underset{\sim}{\Lambda}^t_r(s)$ provided that $\|d\underset{\sim}{\Lambda}^t_r(s)/\, ds\|_h < \infty$ in the sense that $\underset{\sim}{\Lambda}^t_r(s)$ is absolutely continuous, and, the derivative $d\underset{\sim}{\Lambda}^t_r(s)/ds$, which exists almost everywhere, has a finite h-norm.

we shall only insist that it hold for smooth admissible thermodynamic processes. For smooth processes $\underset{\sim}{\Lambda}_r^t(s), \underset{\sim}{g}(t)$ and $\dot{\underset{\sim}{g}}(t)$ may be assigned arbitrarily, but then

$$\underset{\sim}{\Lambda} = \underset{\sim}{\Lambda}_r, \quad \dot{\underset{\sim}{\Lambda}} = -\frac{d}{ds}\underset{\sim}{\Lambda}_r^t(s)\big|_{s=0} \tag{3.22a,b}$$

For smooth processes the result (3.17) still applies. Nothing further can be deduced from (3.18) in a general way, unless we assume that the generalized-stress functional $\underset{\sim}{\Sigma}$ does not depend on the temperature gradient, that is

$$\underset{\sim}{\Sigma} = \underset{\sim}{\Sigma}\,(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}) \tag{3.23}$$

In such a case we make the following deductions from the inequality (3.18):

$$\theta\sigma' \equiv \left\{\underset{\sim}{\Sigma}(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}) - \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda})\right\}\cdot\dot{\underset{\sim}{\Lambda}} + \\ + \delta\psi(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}\big|\frac{d}{ds}\underset{\sim}{\Lambda}_r^t(s)) \geq 0 \tag{3.24}$$

$$\underset{\sim}{q}(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda},\ \underset{\sim}{g})\cdot\underset{\sim}{g} \leq \rho\theta^2\sigma' \tag{3.25}$$

where we shall call σ' the <u>total dissipation</u>. Note that (3.23), (3.24) and (3.25) also apply to adiabatic materials ($\underset{\sim}{q}(t) = \underset{\sim}{o}$) with $\underset{\sim}{g}$ a parameter in $\underset{\sim}{\Sigma}$ and to the special case of homothermal deformations ($\underset{\sim}{g}(t) = \underset{\sim}{o}$).

We have observed that the Clausius-Duhem inequality may be taken to impose restrictions on allowable processes as well as on constitutive equations. We find that there must be a give and take between constitutive equations and allowable processes: the more allowable processes one wishes to consider the greater are the restrictions on the constitutive equations whereas for more general constitutive equations one has fewer allowable processes.

4. Approximation Theory

We introduce the difference past history $\underset{\sim}{\Lambda}_{rd}^t(s)$ defined by

$$\underset{\sim}{\Lambda}_r^t(s) = \underset{\sim}{\Lambda}_{rd}^t(s) + \underset{\sim}{\Lambda}_r \tag{4.1}$$

We may rewrite (3.17) in the form

$$\psi = \psi(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}) = \psi(\underset{\sim}{\Lambda}_{rd}^t(s);\ \underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) \tag{4.2}$$

The form (4.2) can be written even if (4.6) below did not hold, so that by (4.1) the form (4.2) has the property

$$\psi(\underset{\sim}{\Lambda}_{rd}^t(s);\ \underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda}) = \psi(\underset{\sim}{\Lambda}_{rd}^t(s) - \underset{\sim}{\Omega};\ \underset{\sim}{\Lambda}_r + \underset{\sim}{\Omega},\ \underset{\sim}{\Lambda}) \tag{4.3}$$

for arbitrary $\underset{\sim}{\Omega}$. Further, we split (4.2) in the following way:

$$\psi = \psi_o(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) + \psi'(\underset{\sim}{\Lambda}_{rd}^t(s);\ \underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) \tag{4.4}$$

where

$$\psi_o(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) = \psi(\underset{\sim}{O};\ \underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}),\quad \psi'(\underset{\sim}{O};\ \underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) = 0 \tag{4.5a,b}$$

With (4.5b) and the fact that

$$\lim_{s\to\infty}\underset{\sim}{\Lambda}_{rd}^t(s) = \underset{\sim}{O} \tag{4.6}$$

we are in position to apply the Coleman-Noll approximation theorem for functionals [3] to (4.4). We first have to extend the previously postulated assumption of fading memory by assuming that the functional ψ is n-times differentiable in terms of $\underset{\sim}{\Lambda}_{rd}^t(s)$. Then assuming that $\underset{\sim}{\Lambda}_r^t(s)$ is differentiable n-times at s = 0, the Coleman-Noll approximation theorem for slow motions yields

$$\psi \sim \psi_o(\underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda}) + \sum_{(j_1\ldots j_k)}\underset{\sim}{\psi}_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda})(\underset{\sim}{\Gamma}^{j_1},\ldots,\underset{\sim}{\Gamma}^{j_k}) \tag{4.7}$$

where

$$\underset{\sim}{\Gamma}^i = \frac{d^i}{ds^i}\underset{\sim}{\Lambda}_r^t(s)\big|_{s=0} = (-1)^i\frac{d^i}{dt^i}\underset{\sim}{\Lambda}_r \tag{4.8}$$

and each term in the summation is linear in each of the $\underset{\sim}{\Gamma}^i$. For the n-th order approximation the summation in (4.7) is over all sets of integers $(j_1,\ldots j_k)$ satisfying

$$1 \leq j_1 \leq\ldots\leq j_k \leq n,\ j_1 +\ldots+ j_k \leq n \tag{4.9}$$

The asymptotic approximation sign $\sim$ has the following specific meaning in this article: The <u>retardation</u> $\underset{\sim}{\Lambda}_{r\alpha}^t(s)$ of the past history $\underset{\sim}{\Lambda}_r^t(s)$ is defined by

$$\underset{\sim}{\Lambda}_{r\alpha}^t(s) = \underset{\sim}{\Lambda}_r^t(\alpha s),\quad o < \alpha < 1 \tag{4.10}$$

We see that as the <u>retardation factor</u> $\alpha \to 0$ the history varies more and more slowly. Then the Coleman-Noll theorem applied to (4.4) is

$$\psi(\underset{\sim}{\Lambda}_{r\alpha}^t(s);\ \underset{\sim}{\Lambda}) = \psi_o(\underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda}) + \\ + \sum_{(j_1\ldots j_k)}\alpha^{j_1+\ldots+j_k}\underset{\sim}{\psi}_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda})(\underset{\sim}{\Gamma}^{j_1}\ldots\underset{\sim}{\Gamma}^{j_k}) + o(\alpha^n) \tag{4.11}$$

where the summation is governed by (4.9).

It follows from (4.7) that

$$\partial_{\underset{\sim}{\Lambda}}\psi \sim \partial_{\underset{\sim}{\Lambda}}\psi_o\ \ (\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) + \\ + \sum_{(j_1\ldots j_k)}\partial_{\underset{\sim}{\Lambda}}\underset{\sim}{\psi}_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda})(\underset{\sim}{\Gamma}^{j_1},\ldots,\underset{\sim}{\Gamma}^{j_k}) \tag{4.12}$$

Analogous approximations can be written for the generalized-stress functional and for the heat-flow functional. Using the property (4.3) it can be shown that the differential in (3.20) has the approximation form

$$\delta\psi(\underset{\sim}{\Lambda}{}^t_r(s);\ \underset{\sim}{\Lambda}|\frac{d}{ds}\underset{\sim}{\Lambda}{}^t_r(s)) \sim \partial_{\underset{\sim}{\Lambda}_r}\psi_0(\underset{\sim}{\Lambda}_r,\underset{\sim}{\Lambda}) \cdot \underset{\sim}{\Gamma}^1 + \sum_{(j_1\ldots j_k)} \partial_{\underset{\sim}{\Lambda}_r}\psi_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda})(\underset{\sim}{\Gamma}^{j_1}\ldots\underset{\sim}{\Gamma}^{j_k}) \cdot \underset{\sim}{\Gamma}^1 + \sum_{(j_1\ldots j_k)} \psi_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) \sum_{m=1}^{k} (\underset{\sim}{\Gamma}^{j_1},\ldots,\underset{\sim}{\Gamma}^{j_m+1},\ldots\underset{\sim}{\Gamma}^{j_k}) \tag{4.13}$$

We note that on substituting the approximations into (3.18) and taking all summations to the n-th order, all terms in (3.18) have been approximated to order (n + 1).

For the jump history results (3.19), (3.20) and (3.21), we see, first of all, by substituting the approximations in (3.19) that

$$\underset{\sim}{\Sigma}_0\ (\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) = \partial_{\underset{\sim}{\Lambda}}\psi_0(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}), \tag{4.14a,b}$$

$$\underset{\sim}{\Sigma}_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda}) = \partial_{\underset{\sim}{\Lambda}}\psi_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\ \underset{\sim}{\Lambda})$$

The approximation (4.13) must satisfy the inequality (3.20). The approximation for the heat flux must then satisfy (3.21).

For the case of histories smooth at $s = 0$ the approximations must all be substituted in (3.18) which then must be satisfied. Note that even though we consider smooth histories, the jump-history operator $\partial_{\underset{\sim}{\Lambda}}$ may yield non-zero values. We now put the above results in "component" form, that is in terms of the deformation gradient tensor and the temperature. Equation (4.7) becomes

$$\psi \sim \psi_0(\underset{\sim}{F}_r,\ \theta_r,\ \underset{\sim}{F},\ \theta) + \sum_{\substack{(i_1\ldots i_k)\\(j_1\ldots j_k)}} \psi^{i_1\ldots i_k}_{j_1\ldots j_k}(\underset{\sim}{F}_r,\theta_r,\underset{\sim}{F},\theta)(K^{i_1}_{j_1},\ldots,K^{i_k}_{j_k}) \tag{4.15}$$

where the summation is over all sets of indices $(j_1,\ldots,j_k)$ satisfying (4.9) and over all sets of indices $(i_1,\ldots,i_k)$ satisfying

$$i_m = o,1\ ;\ m = 1,\ldots,k \tag{4.16}$$

and where

$$K^o_{j_m} = \underset{\sim}{F}^r_{j_m} = (-1)^{j_m}\frac{d^{j_m}}{ds^{j_m}}\underset{\sim}{F}{}^t_r(s)|_{s=0} \tag{4.17}$$

$$K^1_{j_m} = \theta^r_{j_m} = (-1)^{j_m}\frac{d^{j_m}}{ds^{j_m}}\theta^t_r(s)|_{s=0} \tag{4.18}$$

Each of the terms $\psi^{i_1\ldots i_k}_{j_1\ldots j_k}(\underset{\sim}{F}_r,\theta_r,\underset{\sim}{F}\theta)(\quad)$ is a k-linear function. Appropriate "component" forms of (4.12), (4.13) and the other approximation forms can be written.

5. Thermodynamics of Viscoelastic Fluids

We wish to apply the foregoing theory to viscoelastic fluids. Purely mechanical simple fluids were first defined and discussed by Noll [7]. The generalization of the constitutive equations to include thermodynamics is, following Coleman [1, Sect. 13].

$$f = f(\underset{\sim}{G}^t(s),\ \theta^t(s);\ \rho(t),\ \underset{\sim}{g}(t)),\ f \equiv \psi,\eta,\underset{\sim}{T},\underset{\sim}{q} \tag{5.1a,b,c,d}$$

where

$$\underset{\sim}{G}^t(s) = \underset{\sim}{C}{}^t_t(s) - \underset{\sim}{I},$$
$$\underset{\sim}{C}{}^t_t(s) = (\underset{\sim}{F}{}^t_t(s))^T\underset{\sim}{F}{}^t_t(s),\ \underset{\sim}{F}{}^t_t(s) = \underset{\sim}{F}^t(s)(\underset{\sim}{F}^t(0))^{-1} \tag{5.2}$$

The functionals in (5.1) are isotropic in $\underset{\sim}{G}^t(s)$ and $\underset{\sim}{g}(t)$.

We now define $\underset{\sim}{\Lambda}^t(s)$ to be

$$\underset{\sim}{\Lambda}^t(s) = (\underset{\sim}{G}^t(s),\ \theta^t(s)) \tag{5.3}$$

and Λ to be ordered pair (ρ,θ) with a scalar product defined by

$$\Lambda_1 \cdot \Lambda_2 = \rho_1\rho_2 + \theta_1\theta_2 \tag{5.4}$$

The past history $\underset{\sim}{\Lambda}{}^t_r(s)$ and the quantity $\underset{\sim}{\Lambda}_r$ are again defined according to (3.1) and (3.2). Corresponding to (3.3) we note in particular that

$$\underset{\sim}{G}_r = \lim_{s\to 0}\ \underset{\sim}{G}{}^t_r(s) \neq \underset{\sim}{O} = \underset{\sim}{G}^t(0) \tag{5.5}$$

Now

$$-\frac{d}{ds}\underset{\sim}{G}^t(s)|_{s=0} = \underset{\sim}{A}_1 \tag{5.6}$$

the 1-st Rivlin-Ericksen tensor. Thus

$$\dot{\underset{\sim}{\Lambda}} = (\underset{\sim}{A}_1,\ \dot{\theta}) \tag{5.7}$$

The Clausius-Duhem inequality retains the form (2.23) if the generalized stress is now defined to be

$$\underset{\sim}{\Sigma} = \left(\frac{1}{2\rho}\ \underset{\sim}{T},\ -\ \eta\right) \tag{5.8}$$

Then in terms of past histories the constitutive equations (5.1), can be written in the form

$$f = f\ (\underset{\sim}{\Lambda}{}^t_r(s);\ \Lambda,\ \underset{\sim}{g}),\ f \equiv \psi,\ \underset{\sim}{\Sigma},\ \underset{\sim}{q} \tag{5.9a,b,c}$$

We consider now modifications of the general theory of Sect. 3 which are needed for fluids. We note in (5.2) that $\underset{\sim}{G}{}^t_r(s)$ depends on the time t through the subscript t of $\underset{\sim}{C}^{t}_{rt}(s)$ indicating the changing reference configuration as well as through the history superscript t. It can be easily shown that

$$\underset{\sim}{C}^{t+k}_{r,t+k}(s) = \underset{\sim}{C}^{t}_{rt}(s) - k\underset{\sim}{H}_r(s) + o(k,s) \tag{5.10}$$

where

$$\underset{\sim}{H}_r(s) = \frac{d}{ds}\underset{\sim}{C}^{t}_{rt}(s) + \dot{\underset{\sim}{F}}^{T}\underset{\sim}{F}^{-T}\underset{\sim}{C}^{t}_{rt}(s) + \underset{\sim}{C}^{t}_{rt}(s)\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}} \tag{5.11}$$

Thus (3.8) is replaced by

$$\underset{\sim}{\Lambda}^{t+k}_r(s) = \underset{\sim}{\Lambda}^{t}_r(s) - k\underset{\sim}{\Omega}_r(s) + o(k,s) \tag{5.12}$$

where

$$\underset{\sim}{\Omega}_r(s) = (\underset{\sim}{H}_r(s), \frac{d}{ds}\theta^{t}_r(s)) \tag{5.13}$$

By (5.9a) and (5.12) it follows that (3.13) is replaced by

$$\dot{\psi}(t) = -\delta\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda,\underset{\sim}{g}\mid\underset{\sim}{\Omega}_r(s)) + \partial_\Lambda\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda,\underset{\sim}{g})\cdot\Lambda + \partial_{\underset{\sim}{g}}\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda,\underset{\sim}{g})\cdot\dot{\underset{\sim}{g}} \tag{5.14}$$

It is clear that the equivalent for fluids of the inequality (3.16) yields the result that the free energy cannot depend on the temperature gradient $\underset{\sim}{g}$. Thus (3.18) is replaced by

$$\theta\gamma = \frac{1}{2\rho}\operatorname{tr}\underset{\sim}{T}(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda,\underset{\sim}{g})\underset{\sim}{A}_1 - \eta(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda,\underset{\sim}{g})\dot{\theta} - \partial_\rho\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda)\dot{\rho} - \partial_\theta\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda)\dot{\theta} + \delta\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda|\underset{\sim}{\Omega}_r(s)) - \frac{1}{\rho\theta}\underset{\sim}{q}(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda,\underset{\sim}{g})\cdot\underset{\sim}{g} \ge 0 \tag{5.15}$$

where $\underset{\sim}{\Omega}_r(s)$ is given by (5.13).

We now consider a history with a jump at s = 0. We may choose $\underset{\sim}{\Lambda}^{t}_r(s)$, $\underset{\sim}{F}$, θ, $\dot{\underset{\sim}{F}}$, $\dot{\theta}$ and $\underset{\sim}{g}$ independently. However we see by (5.11) and (5.13) that $\underset{\sim}{\Omega}_r(s)$ depends on $\underset{\sim}{F}$ and $\dot{\underset{\sim}{F}}$ as well as on $\underset{\sim}{\Lambda}^{t}_r(s)$. Since $\underset{\sim}{A}_1$ and $\dot{\rho}$ also depend on $\underset{\sim}{F}$ and $\dot{\underset{\sim}{F}}$ we can deduce no relation on the generalized stress corresponding to (3.19) of the general theory. On the other hand, since $\underset{\sim}{\Omega}_r(s)$ does not depend on $\dot{\theta}$ we can conclude that

$$\eta = \eta(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda) = -\partial_\theta\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda) \tag{5.16}$$

We cannot get relations corresponding to (3.20) or (3.21).

For smooth histories nothing can be deduced from (5.15) unless we assume that the generalized stress does not depend on the temperature gradient, in which case the only conclusions from the inequality (5.15) are

$$\theta\sigma' = \frac{1}{2\rho}\operatorname{tr}\underset{\sim}{T}(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda)\underset{\sim}{A}_1 - \eta(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda)\dot{\theta} - \partial_\rho\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda)\dot{\rho} - \partial_\theta\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda)\dot{\theta} + \delta\psi(\underset{\sim}{\Lambda}^{t}_r(s);\Lambda|\underset{\sim}{\Omega}_r(s)) \ge 0 \tag{5.17}$$

and (3.25) where now σ' is given by (5.17)

6. Approximation Theory for Viscoelastic Fliuds

Basically the approximation theory of Sect. 4 applies to viscoelastic fluids with $\underset{\sim}{\Lambda}$ replaced for the most part by Λ and with $d\underset{\sim}{\Lambda}^{t}_r(s)/ds$ replaced by $\underset{\sim}{\Omega}_r(s)$. The equation corresponding to (4.13) takes on a somewhat different form which can be shown to be

$$\delta\psi(\underset{\sim}{\Lambda}^{t}_r(s),\Lambda|\underset{\sim}{\Omega}_r(s)) \sim \partial_{\underset{\sim}{\Lambda}_r}\psi_0(\underset{\sim}{\Lambda}_r,\Lambda)\cdot\underset{\sim}{\Omega}_r + \sum_{(j_1\ldots j_k)}\partial_{\underset{\sim}{\Lambda}_r}\underset{\sim}{\psi}_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\Lambda)(\underset{\sim}{\Gamma}^{j_1},\ldots,\underset{\sim}{\Gamma}^{j_k})\cdot\underset{\sim}{\Omega}_r + \sum_{(j_1\ldots j_k)}\underset{\sim}{\psi}_{j_1\ldots j_k}(\underset{\sim}{\Lambda}_r,\Lambda)\sum_{m=1}^{k}(\underset{\sim}{\Gamma}^{j_1},\ldots,\underset{\sim}{\Omega}^{j_m},\ldots,\underset{\sim}{\Gamma}^{j_k}) \tag{6.1}$$

where

$$\underset{\sim}{\Omega}_r = (\underset{\sim}{H}_r,\theta_r),\quad \underset{\sim}{H}_r = -\underset{\sim}{A}^{r}_1 + \dot{\underset{\sim}{F}}^{T}\underset{\sim}{F}^{-T}\underset{\sim}{C}^{t}_{rt} + \underset{\sim}{C}^{t}_{rt}\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}} \tag{6.2}$$

and where $\underset{\sim}{\Gamma}^{i}$ is given by (4.8) and $\underset{\sim}{\Omega}^{i}$ is given by

$$\underset{\sim}{\Omega}^{i} = \frac{d^i}{ds^i}\underset{\sim}{\Omega}_r(s)|_{s=0} \tag{6.3}$$

We will list here only the "component" form of (6.1); the "component" forms corresponding to (4.15) and others can be readily written down.

$$\begin{aligned}\delta\psi(\underset{\sim}{G}^{t}_r(s),\theta^{t}_r(s);\rho,\theta|\underset{\sim}{H}_r(s),\tfrac{d}{ds}\theta^{t}_r(s)) &\sim \operatorname{tr}\partial_{\underset{\sim}{G}_r}\psi_0(\underset{\sim}{G}_r,\theta_r,\rho,\theta)\underset{\sim}{H}_r - \partial_{\theta_r}\psi_0(\underset{\sim}{G}_r,\theta_r,\rho,\theta)\theta^{r}_1 \\ &+ \operatorname{tr}\sum_{\substack{(i_1\ldots i_k)\\(j_1\ldots j_k)}}\partial_{\underset{\sim}{G}_r}\underset{\sim}{\psi}^{i_1\ldots i_k}_{j_1\ldots j_k}(\underset{\sim}{G}_r,\theta_r,\rho,\theta)(K^{i_1}_{j_1},\ldots,K^{i_k}_{j_k})\underset{\sim}{H}_r \\ &- \sum_{\substack{(i_1\ldots i_k)\\(j_1\ldots j_k)}}\partial_{\theta_r}\underset{\sim}{\psi}^{i_1\ldots i_k}_{j_1\ldots j_k}(\underset{\sim}{G}_r,\theta_r,\rho,\theta)(K^{i_1}_{j_1},\ldots,K^{i_k}_{j_k})\theta^{r}_1 \\ &+ \sum_{\substack{(i_1\ldots i_k)\\(j_1\ldots j_k)}}\underset{\sim}{\psi}^{i_1\ldots i_k}_{j_1\ldots j_k}(\underset{\sim}{G}_r,\theta_r,\rho,\theta)\sum_{m=1}^{k}(K^{i_1}_{j_1},\ldots,M^{i_m}_{j_m},\ldots K^{i_k}_{j_k})\end{aligned} \tag{6.4}$$

where

$$M^{o}_{j_m} = (-1)^{j_m}\frac{d^{j_m}}{ds^{j_m}}\underset{\sim}{H}_r(s)|_{s=0} = -\underset{\sim}{A}^{r}_{j_m+1} + \dot{\underset{\sim}{F}}^{T}\underset{\sim}{F}^{-T}\underset{\sim}{A}^{r}_{j_m} + \underset{\sim}{A}^{r}_{j_m}\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}} \tag{6.5}$$

and

$$M^{1}_{j_m} = K^{1}_{j_m} \tag{6.6}$$

as given by (4.18).

7. Perfect Fliud Approximation

In Sects. 7, 8 and 9 we shall investigate the restrictions placed on the approximate consititutive equations for viscoelastic fluids by the Clausius-Duhem inequality (5.17). We will assume that the generalized stress is not a function of the temperature gradient and we shall not study here the restrictions placed by (3.25) on the constitutive approximation for the heat flux.

In terms of the retardation factor α of Sect. 4, the approximation theory allows us to write the inequality (5.17) in the form

$$\theta\sigma' = a_o\alpha + o(\alpha) \geq 0 \tag{7.1}$$

where

$$\begin{aligned} a_o = {} & \frac{1}{2\rho}\mathrm{tr}\, \underset{\sim}{T}_o(\underset{\sim}{\Lambda}_r,\Lambda)\underset{\sim}{J}_1 - \frac{1}{3\rho^2}\,\mathrm{tr}\, \underset{\sim}{T}_o(\underset{\sim}{\Lambda}_r,\Lambda)\,\dot{\rho} - \\ & - \eta_o(\underset{\sim}{\Lambda}_r,\Lambda)\dot{\theta} - \partial_\rho\psi_o(\underset{\sim}{\Lambda}_r,\Lambda)\,\dot{\rho} - \\ & - \partial_\theta\psi_o(\underset{\sim}{\Lambda}_r,\Lambda)\dot{\theta} - \mathrm{tr}\,\partial_{\underset{\sim}{G}_r}\psi_o(\underset{\sim}{\Lambda}_r,\Lambda)(\underset{\sim}{J}_1^r - \dot{\underset{\sim}{F}}^T\underset{\sim}{F}^{-T}\underset{\sim}{C}_{rt}^t - \underset{\sim}{C}_{rt}^t\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}}) \\ & + \frac{2}{3\rho_r}\,\mathrm{tr}\,\partial_{\underset{\sim}{G}_r}\psi_o(\underset{\sim}{\Lambda}_r,\Lambda)\dot{\rho}_r - \partial_{\theta_r}\psi_o(\underset{\sim}{\Lambda}_r,\theta)\theta_1^r \end{aligned} \tag{7.2}$$

where $\underset{\sim}{J}_1$ is given by

$$\underset{\sim}{A}_1 = \underset{\sim}{J}_1 - \frac{2}{3}\frac{\dot{\rho}}{\rho}\underset{\sim}{I} \tag{7.3}$$

From (7.1) it follows that

$$\lim_{\alpha\to 0}\frac{1}{\alpha}(\theta\sigma') = a_o \geq 0 \tag{7.4}$$

For histories with a jump at $s = 0$, each of the variables $\Lambda, (\underset{\sim}{J}_1 - \dot{\underset{\sim}{F}}^T\underset{\sim}{F}^{-T}\underset{\sim}{C}_{rt}^t - \underset{\sim}{C}_{rt}^t\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}}), \dot{\rho}, \dot{\theta}, \underset{\sim}{\Lambda}_r, \underset{\sim}{J}_1^r, \dot{\rho}_r, \theta_1^r$ can be varied independently, so that the inequality (7.4) yields the conditions

$$\frac{1}{2\rho}\mathrm{tr}\, \underset{\sim}{T}_o(\underset{\sim}{\Lambda}_r,\Lambda)\underset{\sim}{J}_1 + \mathrm{tr}\,\partial_{\underset{\sim}{G}_r}\psi_o(\underset{\sim}{\Lambda}_r,\Lambda)(\dot{\underset{\sim}{F}}^T\underset{\sim}{F}^{-T}\underset{\sim}{C}_{rt}^t + \underset{\sim}{C}_{rt}^t\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}}) = 0 \tag{7.5}$$

$$\frac{1}{3}\mathrm{tr}\, \underset{\sim}{T}_o(\underset{\sim}{\Lambda}_r,\Lambda) = -\rho^2\partial_\rho\psi_o(\underset{\sim}{\Lambda}_r,\Lambda) \tag{7.6}$$

$$\eta_o(\underset{\sim}{\Lambda}_r,\Lambda) = -\partial_\theta\psi_o(\underset{\sim}{\Lambda}_r,\Lambda) \tag{7.7}$$

$$\mathrm{tr}\,\partial_{\underset{\sim}{G}_r}\psi_o(\underset{\sim}{\Lambda}_r,\Lambda)\underset{\sim}{J}_1^r = 0 \tag{7.8}$$

$$\mathrm{tr}\,\partial_{\underset{\sim}{G}_r}\psi_o(\underset{\sim}{\Lambda}_r,\Lambda) = 0 \tag{7.9}$$

$$\partial_{\theta_r}\psi_o(\underset{\sim}{\Lambda}_r,\Lambda) = 0 \tag{7.10}$$

From (7.10) we conclude that ψ_o is not a function of θ_r. From (7.8) and (7.9) we conclude that ψ_o cannot be a function of $\underset{\sim}{G}_r$. Therefore we have

$$\psi \sim \psi_o(\Lambda) \tag{7.11}$$

Since $\underset{\sim}{T}_o(\underset{\sim}{\Lambda}_r,\Lambda)$ cannot vanish we conclude from (7.5) that it must be isotropic and thus from (7.6) we have

$$\underset{\sim}{T} \sim -\rho^2\partial_\rho\psi_o(\Lambda)\underset{\sim}{I} \tag{7.12}$$

From (7.7) we have

$$\eta \sim -\partial_\theta\psi_o(\Lambda) \tag{7.13}$$

We note that the results (7.11), (7.12) and (7.13) define the classical perfect fluid. Also these results do not depend on the jump (which may be a shock wave as well as an acceleration wave) and therefore it can easily be verified that these results are necessary as well as sufficient conditions that (5.17) be satisfied for smooth histories as well as jump histories.

8. Linear Approximation

Using the results (7.11), (7.12) and (7.13), the approximations for ψ, $\underset{\sim}{T}$ and η to order $n = 1$ are given below. It will be assumed that all coefficients are functions of $\underset{\sim}{\Lambda}_r$ and Λ unless indicated otherwise.

$$\psi \sim \psi_o(\Lambda) + A(\mathrm{tr}\underset{\sim}{A}_1^r) + B\theta_1^r \tag{8.1}$$

$$\underset{\sim}{T} \sim -\rho^2\partial_\rho\psi_o(\Lambda)\underset{\sim}{I} + \frac{1}{2}\lambda\,(\mathrm{tr}\underset{\sim}{A}_1^r)\underset{\sim}{I} + \mu\underset{\sim}{A}_1^r + \alpha\theta_1^r\underset{\sim}{I} \tag{8.2}$$

$$\eta \sim -\partial_\theta\psi_o(\Lambda) + a(\mathrm{tr}\underset{\sim}{A}_1^r) + b\theta_1^r \tag{8.3}$$

We have used the porperty that the above equations must be isotropic in $\underset{\sim}{A}_1^r$.

The conditions (7.5) to (7.10) made a_o in (7.1) vanish. Let us therefore rewrite (7.1) in the form

$$\theta\sigma' = a_1\alpha^2 + o(\alpha^2) \geq 0 \tag{8.4}$$

where

$$\begin{aligned} a_1 = {} & \frac{1}{2\rho}\mathrm{tr}\left[\frac{1}{2}\lambda(\mathrm{tr}\underset{\sim}{A}_1^r)\underset{\sim}{I} + \mu\underset{\sim}{A}_1^r + \alpha\theta_1^r\underset{\sim}{I}\right]\underset{\sim}{A}_1 - \left[a(\mathrm{tr}\underset{\sim}{A}_1^r) + b\theta_1^r\right]\dot{\theta} - \\ & - \left[(\partial_\rho A)(\mathrm{tr}\underset{\sim}{A}_1^r) + (\partial_\rho B)\theta_1^r\right]\dot{\rho} - \left[(\partial_\theta A)(\mathrm{tr}\underset{\sim}{A}_1^r) + (\partial_\theta B)\theta_1^r\right]\dot{\theta} - \\ & - \mathrm{tr}\left[(\partial_{\underset{\sim}{G}_r}A)(\mathrm{tr}\underset{\sim}{A}_1^r) + (\partial_{\underset{\sim}{G}_r}B)\theta_1^r\right](\underset{\sim}{A}_1^r - \dot{\underset{\sim}{F}}^T\underset{\sim}{F}^{-T}\underset{\sim}{C}_{rt}^t - \underset{\sim}{C}_{rt}^t\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}}) - \\ & - \left[(\partial_{\theta_r}A)(\mathrm{tr}\underset{\sim}{A}_1^r) + (\partial_{\theta_r}B)\theta_1^r\right]\theta_1^r - \\ & - A\,\mathrm{tr}(\underset{\sim}{A}_2^r - \dot{\underset{\sim}{F}}^T\underset{\sim}{F}^{-T}\underset{\sim}{A}_1^r - \underset{\sim}{A}_1^r\underset{\sim}{F}^{-1}\dot{\underset{\sim}{F}}) + B\theta_2^r \end{aligned} \tag{8.5}$$

From (8.4) it follows that

$$\lim_{\alpha\to 0}\frac{1}{\alpha^2}(\theta\sigma') = a_1 \geq 0 \tag{8.6}$$

We see immediately that by varying each of $\underset{\sim}{A}_2^r$ and θ_2^r, while holding everything else fixed, we must have

$$A = B = 0 \tag{8.7}$$

Then the inequality (8.6) reduces to

$$a_1 = \frac{1}{2\rho}\mathrm{tr}\left[\frac{1}{2}\lambda(\mathrm{tr}\mathbf{A}_1^r)\mathbf{I} + \mu\mathbf{A}_1^r + \alpha\theta_1^r\mathbf{I}\right]\mathbf{A}_1 - \\ - \left[a(\mathrm{tr}\mathbf{A}_1^r) + b\theta_1^r\right]\dot{\theta} \geq 0 \qquad (8.8)$$

For the jump history case, that is, for acceleration waves, $\mathbf{A}_1$ and $\dot{\theta}$ can be varied independently of everything else, so that it can easily be seen that all the first-order coefficients vanish and the n = 1 case reduces to the perfect fluid. Thus we conclude that the linear fluid cannot satisfy the Clausius-Duhem inequality for arbitrary acceleration waves, which is the well-known result of Duhem for the classical linear viscous fluid [5].

For the smooth history case we drop the superscript r and we have, using $\dot{\theta} \equiv \theta_1$,

$$a_1 = \frac{1}{2\rho}\left[\frac{1}{2}\lambda(\mathrm{tr}\mathbf{A}_1)^2 + \mu\mathrm{tr}\mathbf{A}_1^2\right] + \\ + \left(\frac{\alpha}{2\rho} - a\right)\theta_1\mathrm{tr}\mathbf{A}_1 - b\theta_1^2 \geq 0 \qquad (8.9)$$

where now the coefficients are functions of Λ only. A simple analysis using (7.3) yields the classical results

$$\mu \geq 0, \quad \lambda + \frac{2}{3}\mu \geq 0 \qquad (8.10)$$

as well as the results

$$b \leq 0, \quad \left(\frac{\alpha}{2\rho} - a\right)^2 \leq \frac{-b}{\rho}\left(\lambda + \frac{2}{3}\mu\right) \qquad (8.11)$$

Thus, in summary, we have for n = 1

$$\psi \sim \psi_0(\Lambda) \qquad (8.12)$$

$$\mathbf{T} \sim -\rho^2\partial_\rho\psi_0(\Lambda)\mathbf{I} + \lambda(\Lambda)(\mathrm{tr}\mathbf{A}_1)\mathbf{I} + \mu(\Lambda)\mathbf{A}_1 + \alpha\theta_1\mathbf{I} \qquad (8.13)$$

$$\eta \sim -\partial_\theta\psi_0(\Lambda) + a(\Lambda)\mathrm{tr}\mathbf{A}_1 + b(\Lambda)\,\theta_1 \qquad (8.14)$$

with the restrictions (8.10) and (8.11). We observe that these constitutive equations differ from the traditional constitutive equations for linear fluids because of the possibility of the presence of the last term in (8.13) and the last two terms in (8.14). It must be kept in mind that (8.12), (8.13) and (8.14) is a first-order slow motion approximation to viscoelastic fluids. Whether or not these equations could represent a fluid undergoing rapid motions is a question that remains to be investigated. Thus these equations should be applied with caution to problems such as boundary-layer flow past a semi-infinite plate or "shock structure". Questions concerning various types of approximation to viscoelastic flows and their respective ranges have been discussed recently [8,9].

9. Second-order Approximation

Since the linear approximation does not sustain acceleration waves, we consider only smooth motions here.

From the results (8.10) and (8.11) we see by (8.9) that a_1 is not identically zero. We now rewrite (8.4) in the form

$$\theta\sigma' = a_1\alpha^2 + a_2\alpha^3 + o(\alpha^3) \qquad (9.1)$$

For those cases where a_1 vanishes, that is $\mathbf{A}_1 = \mathbf{0}$ and $\theta_1 = 0$, it follows that

$$\lim_{\alpha\to 0}\frac{1}{\alpha^3}(\theta\sigma') = a_2 \geq 0 \qquad (9.3)$$

We write the second-order approximation to ψ in the form

$$\psi \sim \psi_0 + f(\mathbf{A}_1,\theta_1) + C\,\mathrm{tr}\mathbf{A}_2 + D\theta_2 \qquad (9.4)$$

Then by (6.4) it can be seen that a_2 has the form

$$a_2 = g(\mathbf{A}_1,\theta_1,\mathbf{A}_2,\theta_2) - C\,\mathrm{tr}(\mathbf{A}_2 - \dot{\mathbf{F}}^T\mathbf{F}^{-T}\mathbf{A}_2 - \mathbf{A}_2\mathbf{F}^{-1}\dot{\mathbf{F}}) + D\theta_3 \qquad (9.5)$$

Since every term in g is of degree three, that is the subscripts of the factors in each term must total three, we can see that g vanishes when $\mathbf{A}_1$ and θ_1 vanish. We can conclude that the condition (9.3) requires that

$$C = D = 0 \qquad (9.6)$$

and that there are no other restrictions placed by (9.3).

10. Appendix on Coleman's Difference-History Theory

The difference history $\boldsymbol{\Lambda}_d^t(s)$ of the history $\boldsymbol{\Lambda}^t(s)$ is defined by

$$\boldsymbol{\Lambda}^t(s) = \boldsymbol{\Lambda}_d^t(s) + \boldsymbol{\Lambda}, \quad \boldsymbol{\Lambda} = \boldsymbol{\Lambda}^t(0) = \boldsymbol{\Lambda}(t) \qquad (10.1)$$

Coleman [1,2] writes for the free energy functional

$$\psi = \psi(\boldsymbol{\Lambda}^t(s)) = \psi(\boldsymbol{\Lambda}_d^t(s);\ \boldsymbol{\Lambda}) \qquad (10.2)$$

Coleman [1,(5.4)](see (10.6) below) does not use (10.2) with the restriction that the functional argument vanish at s = 0. Clearly then the right-hand side of (10.2) should have the property

$$\psi(\boldsymbol{\Lambda}_d^t(s);\ \boldsymbol{\Lambda}) = \psi(\boldsymbol{\Lambda}_d^t(s) - \boldsymbol{\Omega};\ \boldsymbol{\Lambda} + \boldsymbol{\Omega}) \qquad (10.3)$$

for arbitrary $\underset{\sim}{\Omega}$.

Now let us examine equation [1, (5.14)] which defines the differential operator ∇ (omitting the dependence on $\underset{\sim}{g}$):

$$\nabla\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}) \cdot \underset{\sim}{\Omega} = \delta\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}|\underset{\sim}{\Omega}^t(s)) \tag{10.4}$$

where $\underset{\sim}{\Omega}^t(s)$ is the constant history

$$\underset{\sim}{\Omega}^t(s) = \underset{\sim}{\Omega}, \quad 0 \le s < \infty \tag{10.5}$$

The right-hand side of (10.4) is defined by [1, (5.4)]:

$$\begin{aligned}&\psi(\underset{\sim}{\Gamma}(s) + \underset{\sim}{\Omega}^t(s);\underset{\sim}{\Lambda})\\ &= \psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}) + \delta\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}|\underset{\sim}{\Omega}^t(s)) + o(\|\underset{\sim}{\Omega}^t(s)\|_h)\end{aligned} \tag{10.6}$$

where the norm $\|\underset{\sim}{\Omega}^t(s)\|_h$ is defined by (3.12). From (10.5) and (3.12) we have

$$\|\underset{\sim}{\Omega}^t(s)\|_h = \|\underset{\sim}{\Omega}\|\left[\int_0^\infty h(s)^2 ds\right]^{\frac{1}{2}} = O(\|\underset{\sim}{\Omega}\|) \tag{10.7}$$

and therefore

$$o(\|\underset{\sim}{\Omega}^t(s)\|_h) = o(\|\underset{\sim}{\Omega}\|) \tag{10.8}$$

Also by (10.5) and the property (10.3), the left-hand side of (10.6) can be written as

$$\psi(\underset{\sim}{\Gamma}(s) + \underset{\sim}{\Omega}^t(s);\underset{\sim}{\Lambda}) = \psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda} + \underset{\sim}{\Omega}) \tag{10.9}$$

Substituting (10.8) and (10.9) in (10.6) we have

$$\begin{aligned}&\psi(\underset{\sim}{\Gamma}(s) + \underset{\sim}{\Omega}^t(s);\underset{\sim}{\Lambda})\\ &= \psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}) + \delta\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}|\underset{\sim}{\Omega}^t(s)) + o(\|\underset{\sim}{\Omega}^t(s)\|_h)\end{aligned} \tag{10.10}$$

But by comparison with [1, (5.5)] we see that

$$\delta\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}|\underset{\sim}{\Omega}^t(s)) = \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}) \cdot \underset{\sim}{\Omega} \tag{10.11}$$

Now comparing (10.4) and (10.11) we see that

$$\nabla\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}) = \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Gamma}(s);\underset{\sim}{\Lambda}) \tag{10.12}$$

That is, the differential operators ∇ and $\partial_{\underset{\sim}{\Lambda}}$ are identical. The main consequence of this result in Coleman's theory is that the generalized stress $\underset{\sim}{\Sigma}$ by [1, (6.24)], is identically zero. Of course, such a result is unacceptable. Let us leave this dilemma for the moment and turn to another point.

Let us examine equations [2, (5.61)]:

$$\psi^* = \psi(\underset{\sim}{\Lambda}_d^t(s) - \underset{\sim}{J}^t(s);\underset{\sim}{\Lambda} + \underset{\sim}{J}) = \psi'^*(\underset{\sim}{J}) \tag{10.13}$$

This equation is supposed to give the value ψ^* of the free energy corresponding to the history $\underset{\sim}{\Lambda}^{t*}(s)$ defined by

$$\underset{\sim}{\Lambda}^{t*}(s) = \begin{cases}\underset{\sim}{\Lambda}^t(0) + \underset{\sim}{J}, & s = 0\\ \underset{\sim}{\Lambda}^t(s), & 0 < s < \infty\end{cases} \tag{10.14}$$

$\underset{\sim}{\Lambda}^{t*}(s)$ is called the jump continuation of $\underset{\sim}{\Lambda}^t(s)$ with jump $\underset{\sim}{J}$. Now applying the property (10.3) we see that (10.13) reduces to

$$\psi^* = \psi(\underset{\sim}{\Lambda}_d^t(s);\underset{\sim}{\Lambda}) \tag{10.15}$$

That is, the free energy is unaffected by a sudden jump. This is a physically unacceptable result. Equation (10.13) was brought about by the equivalence [2,(5.5)]:

$$\underset{\sim}{\Lambda}_d^{t*}(s) = \underset{\sim}{\Lambda}_d^t(s) - \underset{\sim}{J}^t(s), \quad \underset{\sim}{J}^t(s) = \underset{\sim}{J} \tag{10.16}$$

which in turn was due to the use of the norm (3.12).

In the author's opinion, the use of the norm (3.12) for histories with a jump at $s = 0$ is not physically reasonable. Furthermore, it is the use of the norm (3.12) along with our result (10.12) that leads to the previous deduction that the generalized stress is identically zero. Coleman's reasoning on pp. 17 and 18 of [1], which leads to the generalized stress relation [1, (6.24)], hinges on considering a jump in $d\underset{\sim}{\Lambda}^t(s)/ds$ at $s = 0$ and the use of the norm (3.12) with such jump histories.

Acknowledgments

This research was supported by the National Aeronautics and Space Administration Grant NsG-664 and National Science Foundation Grant GK-621. Professor C. Truesdell and Dr. C.-C. Wang made helpful criticisms and comments on several points in Sects. 3 and 5 of an earlier version of this paper.

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Corrigenda and Addenda to

ON THE THERMODYNAMIC AND APPROXIMATION THEORY OF VISCOELASTIC MATERIALS

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Equation (3.8) should be replaced by

$$\underset{\sim}{\Lambda}_r^{t+k}(s) = \begin{cases} \underset{\sim}{\Lambda}(t) + (k-s)\dot{\underset{\sim}{\Lambda}}(t) + o(k-s) \ , & o \le s \le k \\ \underset{\sim}{\Lambda}_r^t(s) - k\frac{d}{ds}\underset{\sim}{\Lambda}_r^t(s) + o(k,s) \ , & k < s < \infty \end{cases} \tag{1}$$

Now the linear functional $\delta\psi$ of (3.11) can be represented by an integral:

$$\delta\psi(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}, \underset{\sim}{g} | \underset{\sim}{\Gamma}(s)) \equiv \int_0^\infty \underset{\sim}{\psi}^1(\underset{\sim}{\Lambda}_r^t(\bar{s}),\ s\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot \underset{\sim}{\Gamma}(s)ds \tag{2}$$

where $\underset{\sim}{\psi}^1(\underset{\sim}{\Lambda}_r^t(\bar{s}),\ s\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g})$ so defined is a functional over $\bar{s}$.

Then (3.13) is replaced by

$$\dot{\psi}(t) = -\delta\psi(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g} |\ \frac{d}{ds}\underset{\sim}{\Lambda}_r^t(s)) + \underset{\sim}{\psi}^1(\underset{\sim}{\Lambda}_r^t(s)\ ,\ 0\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot (\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}_r) +$$
$$+ \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Lambda}_r^t(s)\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot \dot{\underset{\sim}{\Lambda}} + \partial_{\underset{\sim}{g}}\psi(\underset{\sim}{\Lambda}_r^t(s)\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot \dot{\underset{\sim}{g}} \tag{3}$$

(3.16) is replaced by

$$\theta\gamma = \left\{ \underset{\sim}{\Sigma}(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) - \partial_{\underset{\sim}{\Lambda}}\psi(\underset{\sim}{\Lambda}_r^t(s)\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \right\} \cdot \dot{\underset{\sim}{\Lambda}} +$$
$$+ \delta\psi(\underset{\sim}{\Lambda}_r^t(s);\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g} |\ \frac{d}{ds}\underset{\sim}{\Lambda}_r^t(s)) - \underset{\sim}{\psi}^1(\underset{\sim}{\Lambda}_r^t(s)\ ,\ 0;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot (\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}_r) -$$
$$- \frac{1}{\rho\theta}\underset{\sim}{q}\ (\underset{\sim}{\Lambda}_r^t(s)\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot \underset{\sim}{g} - \partial_{\underset{\sim}{g}}\psi(\underset{\sim}{\Lambda}_r^t(s)\ ;\ \underset{\sim}{\Lambda}\ ,\ \underset{\sim}{g}) \cdot \dot{\underset{\sim}{g}} \ge 0 \tag{4}$$

(3.18) is replaced by

$$\theta\gamma = \left\{ \underset{\sim}{\Sigma}(\underset{\sim}{\Lambda}^t_r(s) \; ; \; \underset{\sim}{\Lambda} \, , \, \underset{\sim}{g}) - \partial_{\underset{\sim}{\Lambda}} \psi(\underset{\sim}{\Lambda}^t_r(s) \; ; \; \underset{\sim}{\Lambda}) \right\} \cdot \dot{\underset{\sim}{\Lambda}} \; +$$

$$+ \; \delta\psi(\underset{\sim}{\Lambda}^t_r(s) \; ; \; \underset{\sim}{\Lambda} \,|\, \frac{d}{ds} \underset{\sim}{\Lambda}^t_r(s)) - \psi^1(\underset{\sim}{\Lambda}^t_r(s) \, , \, 0 \; ; \; \underset{\sim}{\Lambda}) \cdot (\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}_r) \; -$$

$$- \frac{1}{\rho\theta} \underset{\sim}{q}(\underset{\sim}{\Lambda}^t_r(s) \; ; \; \underset{\sim}{\Lambda} \, , \, \underset{\sim}{g}) \cdot \underset{\sim}{g} \geq 0 \tag{5}$$

and (3.20) is replaced by

$$\theta\sigma \equiv \delta\psi(\underset{\sim}{\Lambda}^t_r(s) \; ; \; \underset{\sim}{\Lambda} \,|\, \frac{d}{ds} \underset{\sim}{\Lambda}^t_r(s)) - \psi^1(\underset{\sim}{\Lambda}^t_r(s) \, , \, 0 \; ; \; \underset{\sim}{\Lambda}) \cdot (\underset{\sim}{\Lambda} - \underset{\sim}{\Lambda}_r) \geq 0 \tag{6}$$

We observe that the second term in the internal dissipation inequality (6) is non-zero only if shock waves (jumps in $\underset{\sim}{\Lambda}$) occur in the processes under consideration.

The remainder of § 3 is unchanged; several consequent changes should be made in §§ 4, 5, 6 and 7; §§ 8 and 9 are unchanged. Actually from § 4 on is valid if we limit our considerations to processes in which shocks do not occur, but acceleration waves may or may not occur as the case may be in the paper.